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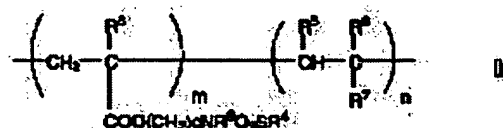
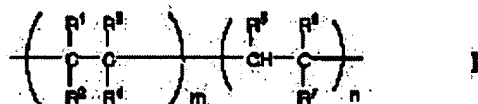
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## (54) REFLECTION PREVENTIVE FILM MATERIAL AND PATTERN FORMING METHOD

## (57)Abstract:

PROBLEM TO BE SOLVED: To enhance the dimensional precision and lamination accuracy by using a fluororesin made of a copolymer of a specified fluorinated vinyl monomer and a vinyl monomer having a hydrophilic group, such as carboxy or sulfo, for a reflection preventive film material.

SOLUTION: A water-soluble fluororesin expressed by formulae I-III is used as a main component. In the formulae I-III, each of R1 and R2 is H or F atom; R3 is H atom or a trifluoromethyl group or the like; R4 is -(CH2)8-(CF2)bX group or the like; R5 is H atom or a carboxy group or the like; R6 is H atom or methyl group or the like; R7 is a carboxy or sulfo group or the like; R8 is H atom or methyl group; R9 is H atom or a 1-6C alkyl group; X is H or F atom; each of (a), (b), and (c) is an integer of 0-2, 1-8, and 2-5, respectively; and a ratio of (m) to (n) is 1:9-9:1.



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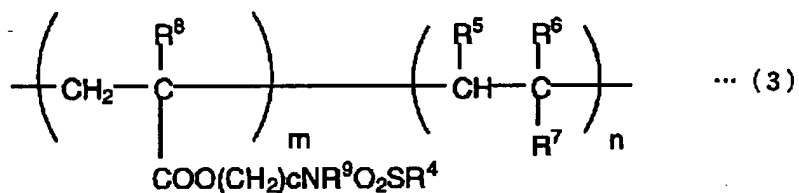
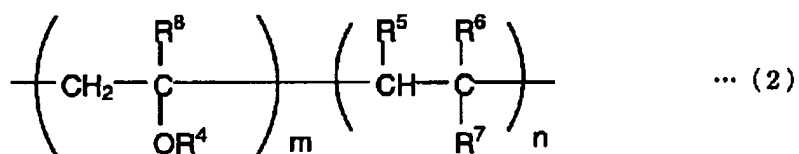
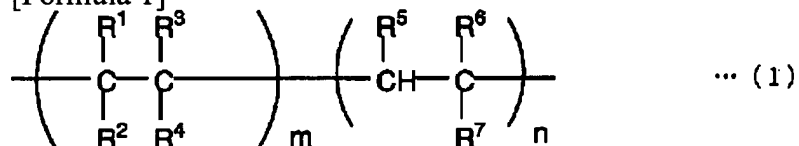
CLAIMS

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## [Claim(s)]

[Claim 1] The antireflection film ingredient characterized by using as a principal component fluororesin meltable in the water shown by following general formula (1) - (3) in the antireflection film which is formed on the photoresist layer formed on the base, and forms the transparent antireflection film removed with a solvent after exposure.

## [Formula 1]



the inside of a formula, and R1 and R2 -- respectively -- a hydrogen atom or a fluorine atom, and R3 -- a hydrogen atom -- -(CH2) a(CF2) bX or -CR ten R11R12, and R5 a fluorine atom, a methyl group or a trifluoromethyl radical, and R4 A hydrogen atom, A methyl group, a carboxyl group, and R6 A hydrogen atom, a methyl group, a carboxyl group, CH2COOH and R7 - A carboxyl group, a sulfonic group, -C(=O) YR13COOH, A hydrogen atom or a methyl group, and R9 C(=O) YR13SO3H and R8 - The straight chain of a hydrogen atom or carbon numbers 1-6, or the alkyl group of the letter of branching, As for at least two of R10-R12, R10-R12 are [ a fluorine atom or a trifluoromethyl radical, and R13 ] the straight chain of carbon numbers 1-6, or the alkylene group of the letter of branching in a hydrogen atom, a fluorine atom, and a trifluoromethyl radical. Moreover, X is a hydrogen atom and a fluorine atom, Y is -O- and -NH-, and, for a, 0-2b are [ the integer of 2-5 and the ratio of m and n of 1-8c ] m:n=1:9-9:1.

[Claim 2] The antireflection film ingredient according to claim 1 characterized by coming to contain at least one or more sorts of a fluorine content organic acid or its amine salt.

[Claim 3] The pattern formation approach characterized by developing a resist layer at the same time an alkali water solution removes an acid-resisting membrane layer after forming an acid-resisting membrane layer and exposing the above-mentioned resist layer by dissolving in water and applying an antireflection-film ingredient according to claim 1 or 2 on the photoresist film.

[Claim 4] The pattern formation approach characterized by forwater removing an acid-resisting membrane layer after forming an acid-resisting membrane layer and exposing the above-mentioned resist layer by dissolving in water and applying an antireflection-film ingredient according to claim 1 or 2 on the photoresist film, and subsequently removing a resist layer with an alkali water solution.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] in manufacture of a semiconductor integrated circuit etc. , especially this invention prevent lowering of the pattern dimensional accuracy produce in order that the laminating of the acid resisting membrane layer may be carry out and exposure light and the reflected light from a substrate may interfere within a photoresist layer on a photoresist layer on the occasion of the photoresist layer formation use at the time of the pattern formation of photolithography , and degradation of the resist pattern configuration by deactivation of the acid in a photoresist layer front face , and relate to the antireflection film ingredient and the resist pattern formation approach of make micro processing possible .

[0002]

[Description of the Prior Art] While detailed-ization of a pattern rule is called for with high integration and high-speed-izing of LSI, development of the further detailed-ized \*\*\*\* serves as pressing need.

[0003] Promising \*\* of the far-ultraviolet-rays lithography is carried out as next-generation ultra-fine processing technology by such background. 0.3-0.4-micrometer processing is also possible for far-ultraviolet-rays lithography, and when the small resist of optical absorption is used, pattern formation with a vertically near side attachment wall becomes possible to a substrate. since [ moreover, ] a pattern imprint can be carried out at a package -- electron-beam lithography -- the through top's point -- advantageous -- as the light source of recent years and far ultraviolet rays -- high -- the technique of using a brightness KrF excimer laser attracts attention.

[0004] However, with the silicon of a substrate ingredient, or other ingredients, if far-ultraviolet-rays light, especially the homogeneous light like a KrF excimer laser are used, since the reflection factor is high, when it is a photoresist layer with high transparency, the interferential action of incident light and the reflected light from a substrate will arise. Since this interferential action fluctuates a pattern dimension to the thickness of a resist layer, the precision of a pattern dimension will be reduced. When irregularity is especially in a substrate, since the thickness of a resist layer changes a lot in a level difference part, it is influenced by light of interference, and the dimensional accuracy of a resist layer falls, and it stops being able to carry out pattern processing at exact size. Furthermore, the dimensional accuracy of the alignment mark for doubling exposure also falls, and the problem of leading to lowering of doubling precision is also produced.

[0005] Moreover, when a chemistry magnification mold resist ingredient performs far ultraviolet rays, an electron ray, and X ray lithography and the case where it is a positive-resist ingredient when the neglect time amount from exposure to PEB (Post Exposure Bake) becomes long is taken for an example, when pattern formation is carried out, a line pattern becomes T-top configuration, namely, it has the problem [referred to as PED (Post Exposure Delay)] that the pattern upper part becomes thick. This is considered for the solubility on the front face of a resist to fall, and serves as a big fault in the case of presenting practical use. For this reason, [W. which spoils a dimension controllability even if it makes dimension control at a lithography process difficult and faces substrate processing using dry etching

Hinsberg, et al., J.Photopolym.Sci.Technol., 6 (4), 535-546(1993)./T.Kumada and et the 1994 spring Japan Society of Applied Physics related rehearsal [ besides al., J.Photopolym.Sci.Technol., and 6(4) 571-574(1993). / Hatanaka ] collection, p567, 29p, and MB-2 reference --] .

[0006] In the chemistry magnification mold resist ingredient, the cause of the problem of PED is considered that the basic compound in an environmental dependency, i.e., air, is involving greatly. Since the acid on the front face of a resist which was generated by exposure in the case of the positive-resist layer reacts with the basic compound in air and deactivates, if the neglect time amount to PEB becomes long, the amount of the acid which deactivates so much will increase and decomposition of an acid instability radical will stop being able to happen easily. Therefore, a surface refractory-ized layer will be formed and a pattern will become T-top configuration.

[0007] then, ARC which forms the antireflection film in multilayer-resist methods (JP,51-10775,A etc.) and a resist lower layer as a pattern formation method which solved the above-mentioned trouble produced with the irregularity on the front face of a substrate -- ARCOR which forms the antireflection film in law (JP,59-93448,A etc.) and the resist upper layer -- law (JP,62-62520,A, No. 62521 official report, etc.) etc. is proposed.

[0008] However, a multilayer-resist method has the trouble that dimensional accuracy falls by the light reflex from an interlayer, while a routing counter increases and productivity worsens, since it is the approach of forming the resist pattern which serves as a mask in a resist layer by performing a pattern imprint two-layer or after carrying out 3 stratification.

[0009] Moreover, since the ARC method is the approach of etching the antireflection film formed in the lower part of a resist layer, its lowering of dimensional accuracy is large, and since an etching process increases, it has the problem that productivity also worsens.

[0010] On the other hand, the ARCOR method is an approach an antireflection film is formed in the upper part of a resist layer, it is an approach including the process which exfoliates after exposure, and is simple and detailed, and dimensional accuracy and doubling precision can form a high resist pattern.

[0011] That is, by using the ingredient which has low refractive indexes, such as perfluoroalkyl compounds, such as a perfluoroalkyl polyether and perfluoro alkylamine, as an antireflection film, the reflected light in a resist layer-antireflection film interface is reduced substantially, and, in the case of JP,62-62520,A, the amount of fluctuation of the pattern dimension of a resist image is stopped to one third compared with a resist monolayer by this.

[0012] However, the above-mentioned perfluoroalkyl compound must dilute with the diluent of fluorine systems, such as chlorofluocarbon, in order to control spreading thickness, since the solubility over an organic solvent is low, and in case it removes the antireflection film containing the above-mentioned perfluoroalkyl compound, chlorofluocarbon etc. is again used for it. Here, although chlorofluocarbon does not cause mutual mixing (INTAMIKISHINGU) with a lower layer resist, the activity poses a problem from a viewpoint of environmental protection now. Furthermore, a routing counter increases, and in order to use a very expensive solvent, it also has industrially the problem of being uneconomical.

[0013] Without starting INTAMIKISHINGU in a resist layer-antireflection-film interface by using the polysaccharide which is water solubility as an antireflection-film ingredient in the case of JP,62-62521,A, since clearance of the antireflection film can be further shared with a development process, it is satisfactory also in process and, moreover, is said that it is simple.

[0014] However, since the refractive index is not low compared with the above-mentioned perfluoroalkyl compound, the amount of fluctuation of a pattern dimension can stop only 2/3 compared with a resist monolayer, and cannot satisfy the above-mentioned polysaccharide.

[0015] Furthermore, an approach given in JP,5-188598,A It consists of the two-component systems with the fluorocarbon compound of the low refractive index which is fusibility or dispersibility in water or an aqueous alkali solution as an antireflection film ingredient in the film plasticity polymer binder which is fusibility or dispersibility, water, or an aqueous alkali solution. Although effectiveness is demonstrated as an antireflection film ingredient of a general-purpose resist using a diazo naphthoquinone compound Since all the fluorocarbon compounds used here have ammonium salt, deactivation of the acid of a chemistry magnification mold resist front face cannot be caused, and the problem of Above PED cannot

be solved.

[0016] So, by the approach given in JP,6-118630,A, as an antireflection film ingredient, among solid content, although 90 % of the weight or more and the proton generating matter are constituted at 10 or less % of the weight among solid content, a water-soluble film formation component Since the refractive index is not low, to the function as an antireflection film ingredient of a chemistry magnification mold resist like the fault of above-mentioned JP,62-62521,A A chip, And degradation of a pattern profile which will be depended superfluously [ supply of an acid ] if the water-soluble inorganic acid currently mentioned as an example of the proton generating matter and an organic acid with small molecular weight are added 10% of the weight or more among solid content takes place. Furthermore, the ammonium weak acid salt currently mentioned as an example of the proton generating matter cannot cause deactivation of the acid of a chemistry magnification mold resist front face, and the problem of Above PED cannot be solved.

[0017] Moreover, an approach given in JP,6-148896,A consists of a polyvinyl-pyrrolidone homopolymer and fluorine content organic-acid ammonium salt as an antireflection-film ingredient, moreover carries out only operation of only a general-purpose resist, and does not solve the problem of PED of the above-mentioned chemistry magnification mold resist ingredient as well as the fault of JP,5-188598,A. Furthermore, since it is a PORIPI nil pyrrolidone homopolymer, and there is no unit which has hydrophobicity, the membrane formation nature on the resist film is bad, and has the fault that a refractive index is also high.

[0018] It is detailed, dimensional accuracy and doubling precision are high, and simple, it was made in view of the above-mentioned situation, productivity is high and forms a resist pattern with sufficient repeatability, it is cheap and this invention aims at offering an antireflection film ingredient safe for an environment, and the pattern formation approach.

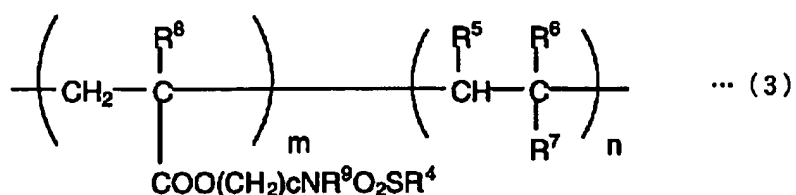
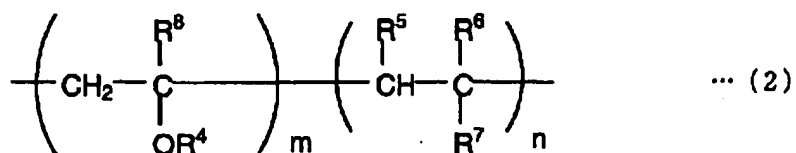
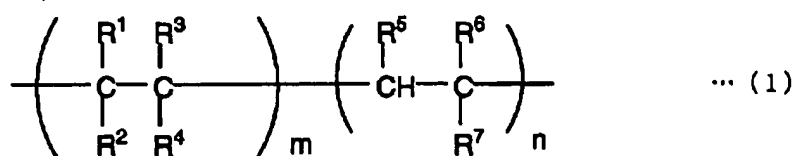
[0019]

[The means for solving a technical problem and the gestalt of implementation of invention] The vinyl monomer which has the fluorine atom which can dissolve in water easily without using a solvent like chlorofluorocarbon as a result of inquiring wholeheartedly, in order that this invention person may attain the above-mentioned object, and is shown by following general formula [ of a low refractive index ] (1) - (3), and a carboxyl group, By using the fluororesin which consists of a copolymer with the vinyl monomer which has a hydrophilic radical called a sulfonic group for an antireflection film ingredient The knowledge of reducing the reflected light in a resist layer front face without loss of incident light, and being able to hold down the amount of fluctuation of the pattern dimension by optical multiplex interference in a resist layer to 1/2 or less compared with a resist monolayer was carried out.

[0020]

[Formula 2]





the inside of a formula, and R1 and R2 -- respectively -- a hydrogen atom or a fluorine atom, and R3 -- a hydrogen atom -- -(CH2) a(CF2) bX or -CR ten R11R12, and R5 a fluorine atom, a methyl group or a trifluoromethyl radical, and R4 A hydrogen atom, A methyl group, a carboxyl group, and R6 A hydrogen atom, a methyl group, a carboxyl group, CH2COOH and R7 - A carboxyl group, a sulfonic group, -C(=O) YR13COOH, A hydrogen atom or a methyl group, and R9 C(=O) YR13SO3H and R8 - The straight chain of a hydrogen atom or carbon numbers 1-6, or the alkyl group of the letter of branching, As for at least two of R10-R12, R10-R12 are [ a fluorine atom or a trifluoromethyl radical, and R13 ] the straight chain of carbon numbers 1-6, or the alkylene group of the letter of branching in a hydrogen atom, a fluorine atom, and a trifluoromethyl radical. Moreover, X is a hydrogen atom and a fluorine atom, Y is -O- and -NH-, and, for a, 0-2b are [ the integer of 2-5 and the ratio of m and n of 1-8c ] m:n=1:9-9:1.

[0021] Moreover, by adding at least one or more sorts of amine salts of a fluorine content organic acid or a fluorine content organic acid to the fluororesin of above-mentioned general formula (1) - (3), the trap of the basic compound in the base in air can be carried out by the sulfonic group and/or fluorine content organic acid of fluororesin which can lower a refractive index further and are shown by above-mentioned general formula (1) - (3), and the problem of PED can be solved.

[0022] Here, the amine salt of a fluorine content organic acid can lower the refractive index of a protective coat, without carrying out deactivation of the acid on the front face of a resist by combining with the fluororesin which has a strong acid radical like a sulfonic group. And since these have large molecular weight, it is hard to diffuse them in a resist layer, and they carry out the knowledge of being useful also as a protective coat of the chemistry magnification mold resist upper layer which can solve the problem of degradation of the resist layer of a pattern profile, and came to make this invention.

[0023] Namely, when film formation is carried out using the fluororesin which consists of a copolymer shown by above-mentioned formula (1) - (3), Since the reflection factor of light can be substantially reduced if it becomes a low refractive index (refractive index; about 1.50 or less) and this film is made into the upper layer of a resist layer When the dimensional accuracy of a resist image can be raised, the amount of fluctuation of the pattern dimension by optical multiplex interference in a resist layer can be held down to 1/2 or less compared with a resist monolayer.

[0024] Moreover, general fluororesin has water repellence, and to dissolving only in a special solvent like chlorofluorocarbon, since the fluororesin shown by above-mentioned formula (1) - (3) has hydrophilic radicals, such as a carboxyl group and a sulfonic group, it dissolves it in water easily. Therefore, insurance and cheap water can perform antireflection film formation easily, and even if it moreover

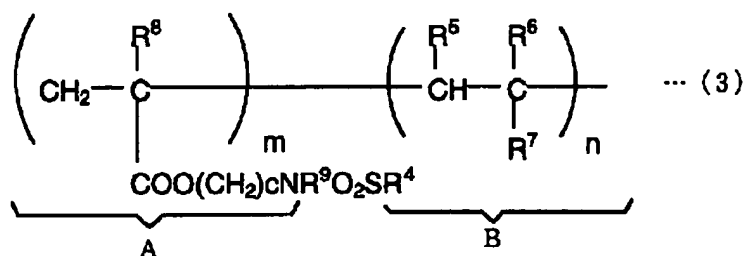
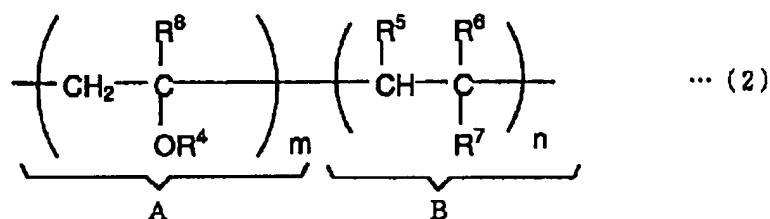
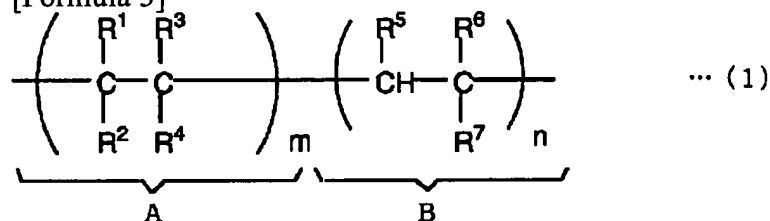
faces clearance of an antireflection film, it can carry out easily and thoroughly using water. Furthermore, since the resin shown by above-mentioned formula (1) - (3) dissolves also in the alkali water solution used for the development of a resist layer easily, it can perform simultaneously the development of a resist layer and the clearance of an antireflection film layer by the alkali water solution, and can shorten a pattern formation process.

[0025] Therefore, by carrying out the laminating of this on a photoresist layer, and forming an acid-resisting membrane layer, degradation of the resist pattern configuration by deactivation of the acid in a photoresist layer front face can be prevented, moreover INTAMIKISHINGU in a resist layer-antireflection-film interface is not started, and a process process is also satisfactory and, as for the antireflection-film ingredient of this invention, safe for an environment.

[0026] Hereafter, it is formed per this invention and also on the photoresist layer which formed this invention on the substrate when explained in detail, and the water shown by following general formula (1) - (3) is provided with the antireflection film ingredient which uses meltable fluororesin as a principal component in the antireflection film ingredient which forms the transparent antireflection film removed with a solvent after exposure.

[0027]

[Formula 3]



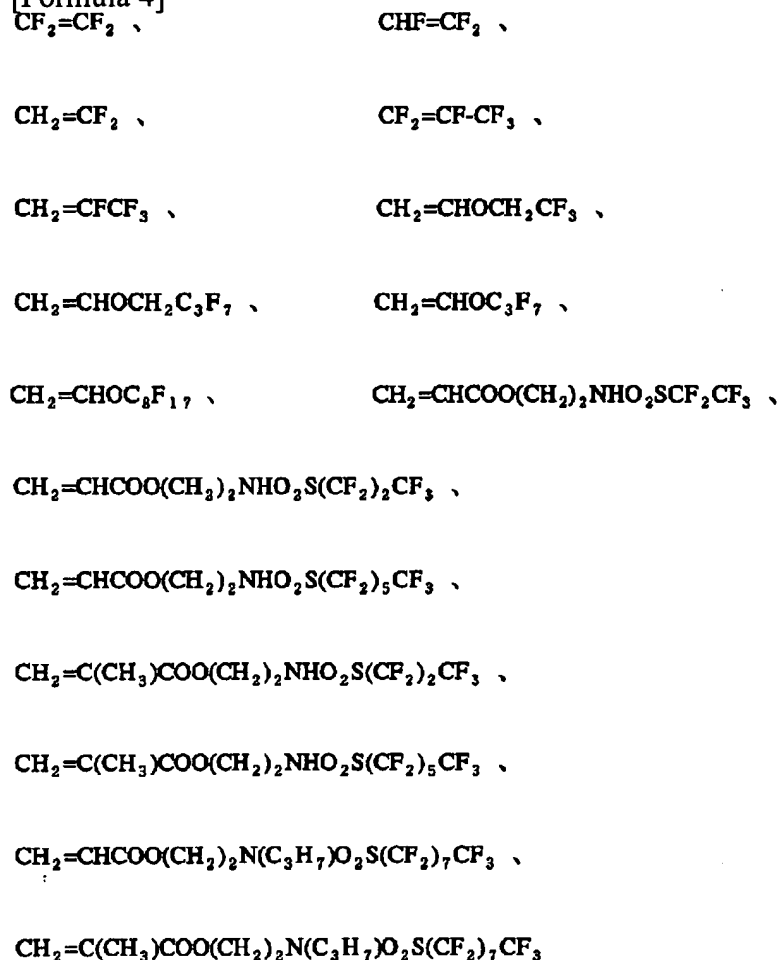
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8c ] m:n=1:9-9:1.

[0028] The above-mentioned formula (1) The fluororesin of - (3) consists of a hydrophilic unit for dissolving in the water and the alkali water solution of a fluorine atom content unit and Above B in which the refractive index of Above A is reduced, and the following can mention it as an A unit monomer.

[0029]

[Formula 4]



[0030] The ratios of m and n which an acrylic acid, a methacrylic acid, an itaconic acid, a maleic acid, a vinyl sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, etc. are mentioned as a B unit monomer, and, on the other hand, show the abundance ratio of the fluorine atom content unit A and the hydrophilic unit B are 1:9-9:1.

[0029] Since it is desirable with 248nm wavelength light that it is [ or more 1 ] 1.5 or less here as for the refractive index of the fluororesin of above-mentioned formula (1) - (3), it is desirable that it is 30 % of the weight or more as for the weight of the fluorine atom occupied to a copolymer for that purpose and its 30 - 60 % of the weight is desirable for becoming still more nearly meltable in water and an alkali water solution, it is desirable to adjust the ratio of m and n so that it may become this range.

[0030] Moreover, since a hydrophobic property becomes strong so that the carbon number of the fluorine atom content unit A and the number of fluorines increase, it is desirable for n to be large for becoming meltable in water and an alkali water solution. For example, by the case where R4 is a tetrafluoro propyl group, the range of m:n=7:3-5:5 becomes the optimal by the case where R4 is a heptadeca fluoro decyl group, to the range of m:n=8:2-6:4 being the optimal in respect of both solubility and a refractive index. A refractive index low enough may not be obtained with in any case, it becoming insoluble in water and an alkali water solution, or refractory, if the ratio of m exceeds the above-

mentioned range, and the ratio of m being under the above-mentioned range. Moreover, when the monomer which has the sulfonamide radical which is a polar group in intramolecular like  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_2\text{NHO}_2\text{S}(\text{CF}_2)_2\text{CF}_3$  as an A unit monomer is used, even if water solubility increases and there is more m a little than the above-mentioned presentation, it is meltable in water and an alkali water solution.

[0031] The fluoro-resin of above-mentioned (1) - (3) which is the principal component of the antireflection-film ingredient of this invention is easily compoundable using the approach of the general radical polymerization of a fluorine atom content vinyl monomer and the vinyl monomer which has a carboxyl group and a sulfonic group etc.

[0032] The above-mentioned formula (1) If it is desirable that the number average molecular weight is 1,000-1,000,000 as for the fluoro-resin of - (3) and it carries out to especially 2,000-20,000, it is more suitable. Membrane formation nature may worsen that number average molecular weight is less than 1,000, if 1,000,000 is exceeded, the solubility of fluoro-resin may fall, and it may become difficult to obtain meltable fluoro-resin in water.

[0033] In this invention, as mentioned above, it is desirable to blend at least one sort of a fluorine content organic acid and its amine salt further. The following can be mentioned as this organic acid and its amine salt.

[0034]

[Formula 5]

$F(CF_2)_pCOOH$	... (4)
$H(CF_2)_pCOOH$	... (5)
$F(CF_2CF_2O)_qCF_2COOH$	... (6)
$F(\underset{\text{CF}_3}{\text{CF}_3}CF_2O)_q\underset{\text{CF}_3}{\text{CF}_3}CF_2COOH$	... (7)
$F(CF_2)_pSO_3H$	... (8)
$H(CF_2)_pSO_3H$	... (9)
$F(CF_2)_pCOO^{-+}NHR^{10}R^{11}R^{12}$	... (10)
$H(CF_2)_pCOO^{-+}NHR^{10}R^{11}R^{12}$	... (11)
$F(CF_2CF_2O)_qCF_2COO^{-+}NHR^{10}R^{11}R^{12}$	... (12)
$F(\underset{\text{CF}_3}{\text{CF}_3}CF_2O)_q\underset{\text{CF}_3}{\text{CF}_3}CF_2COO^{-+}NHR^{10}R^{11}R^{12}$	... (13)
$F(CF_2)_pSO_3^{-+}NHR^{10}R^{11}R^{12}$	... (14)
$H(CF_2)_pSO_3^{-+}NHR^{10}R^{11}R^{12}$	... (15)

(The integer of 4-15 and q of p are the integers of 1-10 among a formula.) R10-R12 are a hydrogen atom or the alkyl group of carbon numbers 1-8, for example, a methyl group, an ethyl group, and its an isopropyl group are desirable. Moreover, even if R10-R12 are mutually the same, they may differ.

[0035] in order that the loadings of solid content which consist of fluororesin and a fluorine content organic acid, or its amine salt may set the thickness of a water-soluble layer as 300-3,000Å (0.03-0.3 micrometers) in this invention -- the whole -- 2 - 15 % of the weight is especially desirable one to 30% of the weight. It becomes [ if the loadings of solid content are not filled to 1% of the weight, thickness will become thinner than 300Å, the acid-resisting effectiveness and a PED protective effect may not no longer be acquired, if 30 % of the weight is exceeded, thickness will become thicker than 3,000Å, and / the burden at the time of an exfoliation process ] large and is not desirable.

[0036] Furthermore, the water-soluble film ingredient of this invention is a mixed water solution which it comes to contain ten to 40% of the weight zero to 50% of the weight still more preferably preferably zero to 60% of the weight among solid content about a fluorine content organic acid or its amine salt 60 to 100% of the weight preferably 40 to 100% of the weight among solid content in fluororesin. If fluororesin is not filled to 40% of the weight, compatibility and membrane formation nature may worsen. That only a complement should add the 248nm refractive index of an antireflection film

although carried out to 1.5 or less, when the refractive index of a fluorine content water solubility polymer is 1.5 or less, it is not necessary to add a fluorine system organic acid.

[0037] In addition, although the antireflection-film ingredient of this invention functions as a protective coat as antireflection film of a chemistry magnification mold resist ingredient, it can be used also as antireflection film of a general-purpose resist layer using a diazo naphthoquinone compound etc.

[0038] In order to form the resist pattern using the antireflection-film ingredient of this invention, the lithography process which can adopt a well-known approach, for example, is shown in drawing 1 can perform. First, a photoresist layer 2 is formed by the approach of a spin coat etc. on the substrates 1, such as a silicon wafer. On this photoresist layer 2, apply the antireflection film ingredient of this invention by the approach of a spin coat etc., and the antireflection film layer 3 is formed. Ultraviolet rays with a wavelength of 190-500nm or an excimer laser 4 is exposed in a desired pattern configuration by cutback projection at the antireflection film layer 3. That is, A part can be exposed in drawing 1 (c), and a resist pattern 5 can be formed by the approach of performing simultaneously clearance and development of an acid-resisting membrane layer using an alkali developer. In addition, after exposure, since the process of resist pattern formation becomes complicated, this approach has a method more desirable [ after removing the antireflection film layer 3 using water, negatives can also be developed using an alkali water solution, but ] of performing clearance and development of an antireflection film simultaneously, using an alkali water solution as the resist pattern formation approach.

[0039] In this case, it is desirable the thickness of 300-2,000Å and to form especially the antireflection film layer 3 in the thickness of 420Å and about 1270Å in the case of 248nm exposure light.

[0040] Since the positive resist was used as a photoresist layer 2 in the example shown in drawing 1 , B part remains as a resist pattern, but if the contrast threshold of predetermined level is shown to the light of predetermined wavelength as a photoresist, both a positive type and a negative mold can be used.

[0041] If here explains the light-scattering reduction effectiveness of the antireflection film by the antireflection film ingredient of this invention with reference to drawing 2 and 3, as shown in drawing 2 , only by forming the resist layer 2 in a substrate 1 While the echo (Ir1) with incident light I0 remarkable at an air-resist layer interface takes place and the amount of incident light loses Since it is repeated that the light which entered in the resist layer 2 reflects by the resist layer-substrate interface (Ir2), and this reflected light Ir2 reflects again by the resist layer-air interface (Ir3), an optical multiplex interference arises in a resist layer.

[0042] On the other hand, as shown in drawing 3 , the reflected light Ir4 in the air-antireflection film layer interface of incident light I0 and the reflected light Ir5 in an antireflection film layer-resist interface can be reduced by forming the antireflection film layer 3 of this invention on the resist layer 2. Thus, since the reflected lights Ir4 and Ir5 can be reduced, loss of the amount of incident light decreases, and since the reflected lights Ir6 and Ir7 have the reverse phase of light, it weakens each other, and an optical multiplex interference within the resist layer 2 is controlled.

[0043] That is, the reflection factor (gain) of this acid resisting is reduced, so that it will bring refractive-index  $n'$  of an antireflection film close to  $\sqrt{n}$  and that thickness will be close brought by odd times  $\lambda/4n'$  from the principle of acid resisting, if wavelength of  $n$  and exposure light is set to  $\lambda$  for the refractive index to the exposure light of a resist.

[0044] If it follows, for example, the refractive index in the wavelength same as a chemistry magnification resist ingredient as the ingredient of the polyhydroxy styrene system whose refractive index with a wavelength of 248nm is about 1.78 carries out pattern formation with a KrF excimer laser with a wavelength of 248nm using the antireflection film ingredient of this invention which is about 1.43, odd times of about 430 Å will become the optimal thickness of an antireflection film. In this case, the reduction effectiveness of the above-mentioned reflected light and optical multiplex cross protection are demonstrated effectively.

[0045]

[Effect of the Invention] The antireflection-film ingredient of this invention is useful as a protective coat ingredient as an ingredient which forms the antireflection film which reduces the reflected light in a resist layer front face without loss of incident light, and reduces the amount of fluctuation of the pattern

dimension by optical multiplex interference in a resist layer.

[0046]

[Example] Although a synthetic example, an example, and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example.

[0047] [Synthetic example 1] It added to methanol 250g as 20.7g of 2-acrylamido-2-methyl propane sulfonic acid, and a solvent, and added to the synthetic autoclave of Pori (vinylidene fluoride-co-2-acrylamide-2-methyl-1-propane sulfonic acid) (resin 1) 2.4g of tert-butyl peroxy-2-ethylhexanoate as a catalyst. The system was sealed after deaerating by carrying out bubbling of the desiccation nitrogen, agitating with for [ sufficient ] about 15 minutes. It heated at 80 degrees C, having added in the system and agitating about 60g of vinylidene fluorides well, and the polymerization was performed for 6 to 7 hours. Next, after fully cooling the system of reaction and suspending a polymerization, the obtained reaction solution was poured in into the hexane and resin was isolated. Furthermore, reprecipitation and washing were repeated and refined and Pori (vinylidene fluoride-co-2-acrylamide-2-methyl-1-propane sulfonic acid) 78.0g was obtained. The presentation of the obtained resin was checked by <sup>1</sup>H-NMR and elemental analysis. The presentation ratio of vinylidene fluoride and a 2-acrylamide-2-methyl-1-propane sulfonic acid was about 9:1.

[0048] 7.2g of acrylic acids was used instead of the 2-acrylamide-2-methyl-1-propane sulfonic acid as a monomer which carries out a synthetic polymerization in [synthetic example 2] Pori (vinylidene fluoride-co-acrylic acid) (resin 2), and also copolymerization was performed by the same approach as the synthetic example 1, and Pori (vinylidene fluoride-co-acrylic acid) 65.2g was compounded. The presentation ratio of vinylidene fluoride and an acrylic acid was about 9:1.

[0049] It added to methanol 300g as 1H and 1H-heptafluoro butyl vinyl ether 226.0g, 82.9g of 2-acrylamido-2-methyl propane sulfonic acid, and a solvent, and added to the synthetic autoclave of [synthetic example 3] Pori (1H, 1H-heptafluoro butyl vinyl ether-co-2-acrylamide-2-methyl-1-propane sulfonic acid) (resin 3) 3.2g of tert-butyl peroxy-2-ethylhexanoate as a catalyst. The system was sealed after deaerating by carrying out bubbling of the desiccation nitrogen, agitating with for [ sufficient ] about 15 minutes. The system was heated at 80 degrees C, agitating well, and the polymerization was performed for 6 to 7 hours. Next, the polymer was isolated and refined by the synthesis method 1 and the same approach, and Pori (1H, 1H-heptafluoro butyl vinyl ether-co-2-acrylamide-2-methyl-1-propane sulfonic acid) 170.5g was obtained. The presentation ratio of 1H and 1H-heptafluoro butyl vinyl ether and a 2-acrylamide-2-methyl-1-propane sulfonic acid was about 5:5.

[0050] As a monomer which carries out a synthetic polymerization in [synthetic example 4] Pori (N-(beta-acryloxyethyl) perfluoro octane sulfonamide-co-2-acrylamide-2-methyl-1-propane sulfonic acid) (resin 4) N-(beta-acryloxyethyl) perfluoro octane sulfonamide 179.1g, As 41.5g of 2-acrylamide-2-methyl-1-propane sulfonic acids, and a solvent, methanol 660g, Used 6.6g of tert-butyl peroxy-2-ethylhexanoate as a catalyst, and also copolymerization is performed by the same approach as the synthetic example 3. 219.5g of Pori N-(beta-acryloxyethyl) perfluoro octane sulfonamide-co-2-acrylamide-2-methyl-1-propane sulfonic acids was compounded. The presentation ratio of N-(beta-acryloxyethyl) perfluoro octane sulfonamide and a 2-acrylamide-2-methyl-1-propane sulfonic acid was about 6:4.

[0051] The resist pattern was formed according to the lithography process shown in drawing 1 as a [example 1] antireflection film ingredient using 3.0% water solution of the resin 1 compounded in the synthetic example 1. first, the substrate 1 which consists of a silicon wafer etc. -- SEPR-X04 (the Shin-Etsu Chemical [ Co., Ltd. ] Co., Ltd. make --) Perform prebaking (100 degrees C, 90 seconds) behind a spin coat for a positive resist, and the resist layer 2 is formed ( drawing 1 (a)). Next, on the resist layer 2, the spin coat of the above-mentioned antireflection film ingredient was carried out, the acid-resisting layer 3 was formed by 420A of thickness, and 1,270A ( drawing 1 (b)), and the 248nm KrF excimer laser light 4 was selectively exposed into A part by cutback projection ( drawing 1 (c)). Heat treatment was performed after carrying out predetermined time neglect of this wafer (90 degrees C, 90 seconds). Next, clearance and development of an acid-resisting membrane layer were simultaneously performed using the alkali developer, and the resist pattern 5 was formed ( drawing 1 (d)). The obtained resist

pattern was able to reduce the 0.30-micrometer line dimension variation accompanying fluctuation of resist thickness which had about 900A by about 400A with photoresist monolayer lithography, without starting INTAMIKISHINGU in an interface with a photoresist. Moreover, the resist pattern configuration was good irrespective of the time amount from exposure to PEB, and degradation of the resist pattern configuration of formation of a surface refractory layer was not observed.

[0052] The same result was obtained as a result of performing resist pattern formation by the same approach as an example 1 as a [example 2] antireflection film ingredient using 3.0% water solution of the resin 2 compounded in the synthetic example 2.

[0053] The same result was obtained as a result of performing resist pattern formation by the same approach as an example 1 as a [example 3] antireflection film ingredient using 3.0% water solution of the resin 3 compounded in the synthetic example 3.

[0054] The same result was obtained as a result of performing resist pattern formation by the same approach as an example 1 as a [example 4] antireflection film ingredient using 3.0% water solution of the resin 4 compounded in the synthetic example 4.

[0055] As a [example 5] antireflection-film ingredient, resist pattern formation was performed by the same approach as an example 1 using 5.0% of the weight of the water solution to 60 % of the weight (tetrafluoroethylene-co-2-acrylamide-2-methyl-1-propane sulfonic acid) (presentation ratio 8:2) of Pori, and EF-101 (MITSUBISHI MATERIALS CORP. Make, Perfluorooctanesulfonic acid) 40 % of the weight solid content. The obtained resist pattern was able to reduce the 0.30-micrometer line dimension variation accompanying fluctuation of resist thickness which had about 900A by about 300A with photoresist monolayer lithography, without starting INTAMIKISHINGU in an interface with a photoresist. Moreover, the resist pattern configuration was good irrespective of the time amount from exposure to PEB, and degradation of the resist pattern configuration of formation of a surface refractory layer was not observed.

[0056] As a [example 6] antireflection-film ingredient, in 60 % of the weight (1H, 1H-heptafluoro butyl vinyl ether-co-2-acrylamide-2-methyl-1-propane sulfonic acid) (presentation ratio 4:6) of Pori, and EF-101, as a result of performing resist pattern formation by the same approach as an example 5 using 5.0% of the weight of a water solution to 40% of the weight of solid content, the same result was obtained.

[0057] As a [example 7] antireflection-film ingredient, 40% of the weight of solid content is received in 60 % of the weight (N-(beta-acryloxyethyl) perfluoro octane sulfonamide-co-2-acrylamide-2-methyl-1-propane sulfonic acid) (presentation ratio 4:6) of Pori, and EF-101. The same result was obtained as a result of performing resist pattern formation by the same approach as an example 5 using 5.0% of the weight of a water solution.

[0058] As [example 8] antireflection film, 60 % of the weight (N-(beta-acryloxyethyl) perfluoro octane sulfonamide-co-2-acrylamide-2-methyl-1-propane sulfonic acid) (presentation ratio 4:6) of Pori, 5.0% of the weight of a water solution is used to C-5800 (made in [ Daikin Fine chemical Lab ], 9 H-Hexadecafluorononanic acid) 40 % of the weight solid content. The same result was obtained as a result of performing resist pattern formation by the same approach as an example 5.

[0059] As [example 9] antireflection film, 60 % of the weight (N-(beta-acryloxyethyl) perfluoro octane sulfonamide-co-2-acrylamide-2-methyl-1-propane sulfonic acid) (presentation ratio 4:6) of Pori, The same result was obtained as a result of performing resist pattern formation by the same approach as an example 5 using 5.0% of the weight of a water solution to FC-93 (Sumitomo 3 M company make, Ammonium perfluorooctanesulfonate) 40 % of the weight solid content.

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[Translation done.]



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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is a sectional view explaining the lithography process using the antireflection film ingredient of this invention.

[Drawing 2] It is a sectional view explaining the light-scattering condition of the resist layer which does not form the antireflection film.

[Drawing 3] It is a sectional view explaining the light-scattering condition of the resist layer using the antireflection-film ingredient of this invention.

[Description of Notations]

1 Substrate

2 Photoresist Layer

3 Antireflection Film Layer

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[Translation done.]